POTENTIAL OF PHENOTHIAZINE AS A THIN FILM DOSIMETER FOR UV-A EXPOSURES[1]

A.V. Parisi[a,*], M.G. Kimlin[b], D.J. Turnbull[a,b] & J. Macaranas[b]

[a]Centre for Astronomy, Solar Radiation and Climate, Faculty of Sciences, University of Southern Queensland, Toowoomba, AUSTRALIA. 4350.

[b]Centre for Health Research, School of Public Health, Queensland University of Technology, Brisbane, QLD, AUSTRALIA.

*To whom correspondence should be addressed

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Summary

The research reported in this paper on the changes in absorbance and the calibration of a proposed UVA (320-400 nm) dosimeter have established the phenothiazine/mylar combination as a potential UVA dosimeter for population studies of UVA exposures. The change in optical absorbance at 370 nm was employed to quantify the UVA exposures. This change starts to saturate at approximately 0.3. This relates to solar UVA exposures at a sub-tropical site on a horizontal plane of approximately three to four hours. The shape of this calibration curve varies with the season. This can be overcome in the same manner as for polysulphone where the dosimeter is calibrated for the conditions that it will be employed to measure the UVA exposures.

Introduction

Dosimeters based on polysulphone[1] for measuring the UV wavelengths shorter than 330 nm have been widely employed. These have been calibrated for the measurement of the erythemal UV exposures.[2] Polysulphone dosimeters have been employed in the measurement of UV exposures during normal daily activities to different population groups.[3-8]

The damaging effects and premature photoageing of human skin due to cumulative exposures to the longer UVA wavelengths (320 – 400 nm) have been reported.[9,10] A predominance of UVA mutations in the basal cell layer of human skin have been reported,[11] implicating UVA as a potential carcinogen in human skin. The longer wavelengths of the UVA also penetrate to a greater depth in human skin.[12]

For solar UV, the UVA irradiances are higher than the UVB irradiances by approximately a factor of 100.[13] Additionally, the ratio of the UVA to the erythemal UV irradiances is lower for smaller solar zenith angles (SZA) and higher for the larger SZA. The ratio of UVA to UVB is significantly increased when the solar UV is filtered through untinted glass for environments such as behind glass in an office or greenhouse and in a car with the windows wound up.[14-18]

The prevalence of the UVA and the potential damaging influences of the UVA wavelengths require research on the UVA exposures to various population groups in different environments. These population exposure studies will require a convenient, easy to process and unobtrusive dosimeter that is responsive to only the UVA wavelengths. Several dosimeters responsive to the UVA have been proposed.[19-22] However, these require more processing or analysis compared to the simplicity of use of polysulphone. This paper will present the properties and characteristics of a dosimeter that is responsive to the UVA wavelengths and that is simple to use and analyse so that it can be employed in large scale population UVA exposure studies.

Materials and methods

Dosimeter production

A dosimeter sensitive to the UVA wavelengths was developed for this project. This was based on the chemical phenothiazine cast in thin film form.[23] A dosimeter based on this chemical is sensitive to both the UVA and the UVB waveband. In order to

produce a dosimeter that responds to the UVA wavelengths only, it was filtered with a second thin film that transmits predominantly the UVA and does not transmit the UVB.[24] The filter material employed for this purpose was mylar film with a thickness of approximately 0.13 mm (Cadillac Plastics, Australia).

The optical transmission of the mylar was measured in a UV spectrophotometer (model 1601, Shimadzu Co., Kyoto, Japan) from 280 to 400 nm in 1 nm increments and three scans of the transmission undertaken with the mylar placed normal to the spectrophotometer beam. For these spectrophotometric measurements and subsequent ones presented in this research, the post-exposure measurements have all been undertaken immediately post-exposure of the sample in order to ensure consistency. The previous use of mylar for UVB exclusion in plant effects research has shown that mylar deteriorates and the UVA transmission decreases over a period of approximately a week due to UV radiation.[25] The UVA dosimeter is intended to be employed to measure the UVA exposures for periods of less than one day. Over this period, the amount of deterioration of the mylar is expected to be significantly less. In order to investigate if there is any significant change in the transmission of the mylar, the spectral transmission was measured pre-exposure and post-exposure to solar UV on 6 May 2005 for periods of 2 h, 3 h and 7 h.

The phenothiazine undergoes a change in optical absorbance (ΔA) as a result of exposure to UV radiation.[23] The influence of solar UV on the phenothiazine was investigated by measuring the spectral transmission from 280 to 400 nm in 1 nm increments for the un-exposed phenothiazine and measuring the transmission again after exposure of the dosimeter on a horizontal plane for 75 min. The UVA dosimeter was fabricated by mounting the phenothiazine in thin film form in a 3 cm x 3 cm holder constructed from PVC sheeting with a thickness of several mm. This holder has an opening of approximately 1.2 cm x 1.6 cm (Figure 1). The thickness of the film was uniform and of the order of 20 μm. The mylar was then mounted over the phenothiazine with adhesive labels so that no UV reached the phenothiazine without first passing through the mylar.

The change in optical absorbance of the UVA dosimeter was investigated by measuring firstly the pre-exposure absorbance from 280 to 400 nm in the spectrophotometer. The dosimeters were exposed to 20 min, 60 min and 90 min of solar UV on 17 January and the post exposure optical absorbance measured. The effect of the visible radiation on the dosimeter was estimated by employing a UG11 (Solar Light Co., PA, USA) filter over a dosimeter to act as a broadband UVA filter. The pre- and post-exposure absorbances at 370 nm were measured for two UVA dosimeters. Both dosimeters were exposed simultaneously to 30 minutes of solar radiation, one with the UG11 filter over the opening of the filter and one without.

Calibration

The calibration of the dosimeters was undertaken by exposing a series of dosimeters to differing exposures on a horizontal plane while concurrently measuring the exposures with a UVA meter (model 501, Solar Light Co., PA, USA) that is permanently installed on an unshaded roof (Figure 1) of a building at the University of Southern Queensland, Toowoomba, Australia (27.6 ^{o}S, 151.9 ^{o}E). This calibration relates the UVA exposures to the changes in optical absorbance. The UVA meter is temperature stabilised to 25 ^{o}C and it records the horizontal plane UVA exposures

every five minutes. It is calibrated twice a year to a spectroradiometer mounted on the same unshaded roof and measuring the solar UV spectrum in 0.5 nm increments for every 5 minutes. This spectroradiometer is housed in an environmentally sealed container with temperature stabilisation and it has calibration traceable to the National Physical Laboratory, UK standard.[26] A calibration of the spectroradiometer is undertaken every six months and a stability check of the instrument is undertaken regularly.

The UVA dosimeters were calibrated for a low solar zenith angle (SZA) range in summer on 21 January between 7.55 am and 11.55 am with a SZA range of 57^o to 8^o respectively. Additionally, they were calibrated for a high SZA range on 6 May between 9.25 am and 2.35 pm with the maximum and minimum SZA in this interval of 56^o and 44^o respectively. Dosimeters were exposed for intervals of 5, 10, 15, 20, 30, 45, 60, 90, 120, 180, 210 and 310 min. For each of these dosimeters the absorbance was measured pre-exposure and immediately post-exposure at 370 nm for 4 sites over the dosimeter. The four sites were obtained by rotating each dosimeter by ninety degrees between each measurement about an axis parallel to the spectrophotometer beam.

Results

Dosimeter

The spectral transmission of the mylar before exposure to solar UV and after exposure for periods of 2 h, 3 h and 7 h are provided in Figure 2. The transmission of the filter drops quickly to zero for wavelengths shorter than 320 nm. The small slope in the transmission for wavelengths longer than 320 nm is taken into account in the calibration of the dosimeter. For the 2 h exposure there is no difference between the pre- and post-exposure transmission. There are minor differences for the 3 h and 7 h exposures, however at 400 nm, these are less than 3%. The presented transmission data is the average at each wavelength of four spectral scans of the mylar. The standard deviation at each wavelength of these scans is of the same order of magnitude as these differences.

The spectral transmission of the phenothiazine pre- and post-exposure to solar UV is provided in Figure 3. The largest change in optical transmission occurs at two wavebands, namely in the UVB and the UVA. The fabricated UVA dosimeter is shown in Figure 1 next to the UVA meter. The mylar filter that is employed is lightweight and unobtrusive and would not interfere with the versatility of the dosimeter. The spectral absorbances of the combined phenothiazine/mylar dosimeter to produce the UVA dosimeter measured pre-exposure and post-exposure to 20 min, 60 min and 90 min of solar UV on 17 January are provided in Figure 4. This data shows that the largest ΔA occurs at a wavelength of approximately 370 nm or longer. Consequently, 370 nm has been selected for the determination of the calibration of the UVA dosimeter and for the use as a dosimeter.

The ΔA at 370 nm for the dosimeters that were exposed with and without the broadband UVA filter were within 6.5% of each other. Consequently, the effect of the visible waveband on the ΔA measured at 370 nm is considered to be within the error associated with measuring the UVA radiation with the dosimeter.

Calibration

The calibration graphs for the low SZA and high SZA cases are provided in Figure 5. The data points are the averages of the four ΔA's measured for each dosimeter and the error bars on the x-axis values are the standard deviation of the four measurements. An exponential expression has been fitted to the calibration data for the low SZA case of the form:

$$UVA = 14.99e^{16.66\Delta A} \quad \text{kJ/m}^2$$

with an R^2 value for this expression of 0.99 and where UVA is the UVA exposures in units of kJ/m^2. For the high SZA, the calibration expression has the form:

$$UVA = 9.04e^{17.61\Delta A} \quad \text{kJ/m}^2$$

with an R^2 value for this expression of 0.98.

Discussion

Population studies of the UVA exposures to humans during normal daily activities have not yet been widely undertaken. The research reported in this paper on the changes in absorbance and the calibration of a proposed UVA dosimeter have established the phenothiazine/mylar combination as a potential UVA dosimeter for population studies of UVA exposures. The size and lightweight properties of the dosimeter means that it can be attached to different anatomical sites to measure the UVA exposures to those sites. The change in the optical transmission of the mylar filter due to UV exposures up to seven hours is minimal and if there are any changes they will be incorporated in the calibration of the dosimeter.

The usage of the dosimeter requires the calibration against a calibrated UVA meter. The shape of this calibration curve varies with the season. This can be overcome in the same manner as for polysulphone where the dosimeter is calibrated for the conditions that it will be employed to measure the UVA exposures. The change in optical absorbance at 370 nm of the dosimeter starts to saturate at approximately 0.3. This relates to solar UVA exposures at a sub-tropical site on a horizontal plane of approximately three to four hours. For the case of filtered UV through building window glass or car window glass, the period of exposure before the response begins to saturate may be different. This will be investigated further in future research.

Acknowledgements

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Figure Captions

Figure 1 – The UVA dosimeter next to the UVA meter employed for the calibration of the dosimeters.

Figure 2 – The spectral transmission of the mylar before exposure to solar UV and after exposure to periods of (a) 2 h, (b) 3 h and (c) 7 h (The before and after exposure curves are overlapping for the 2 h and 3 h exposures).

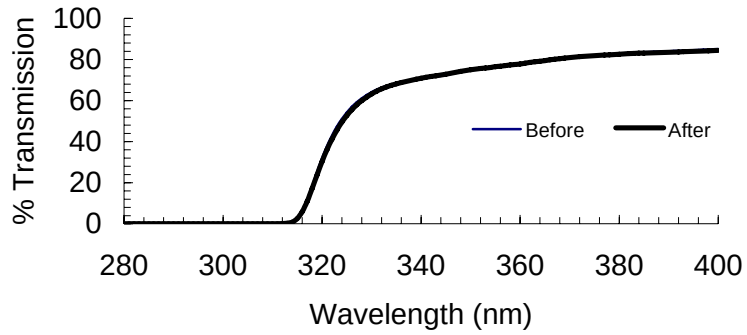
Figure 3 – The optical transmission of the phenothiazine before and after exposure to 75 minutes of solar UV on a horizontal plane.

Figure 4 – Spectral absorbance of the UVA dosimeter measured pre-exposure and post-exposure to 20 min, 60 min and 90 min (from bottom to top curve) of solar UV on 17 January.

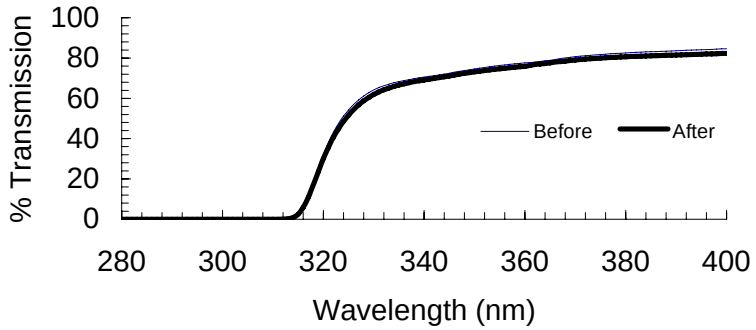
Figure 5 – (a) Low SZA calibration for the UVA dosimeter and (b) a high SZA calibration.

Figure 1 – The UVA dosimeter next to the UVA meter employed for the calibration of the dosimeters.

(a)



(b)



(c)

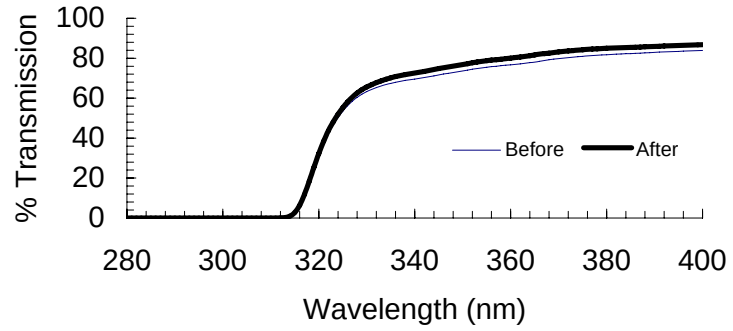


Figure 2 – The spectral transmission of the mylar before exposure to solar UV and after exposure to periods of (a) 2 h, (b) 3 h and (c) 7 h (The before and after exposure curves are overlapping for the 2 h and 3 h exposures).

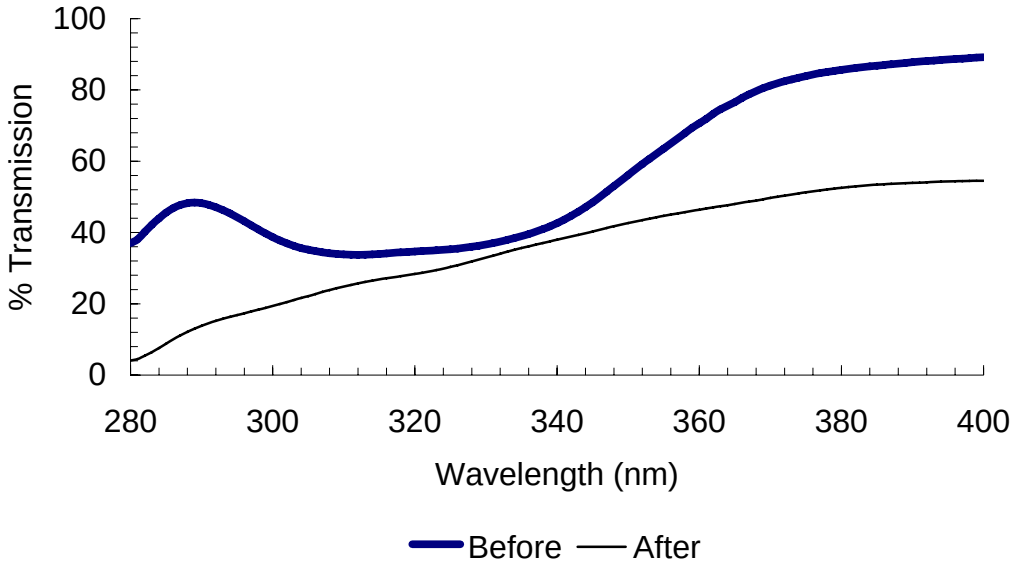


Figure 3 – The optical transmission of the phenothiazine before and after exposure to 75 minutes of solar UV on a horizontal plane.

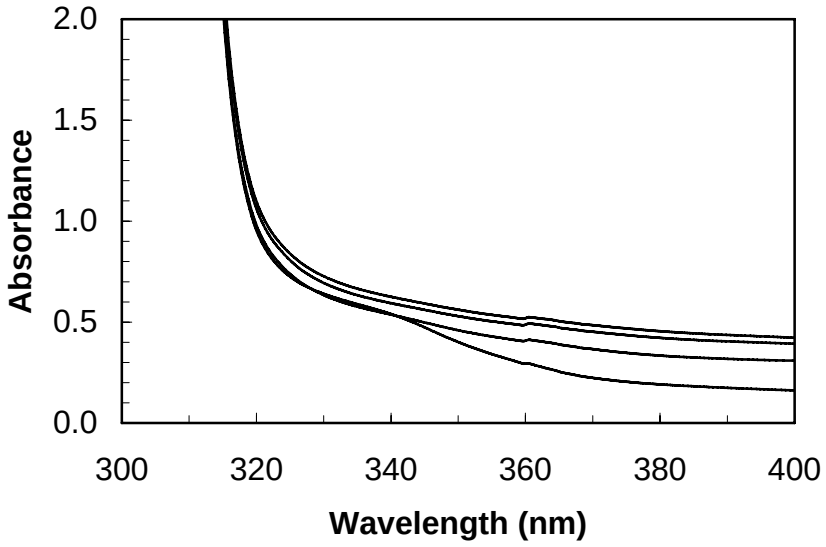
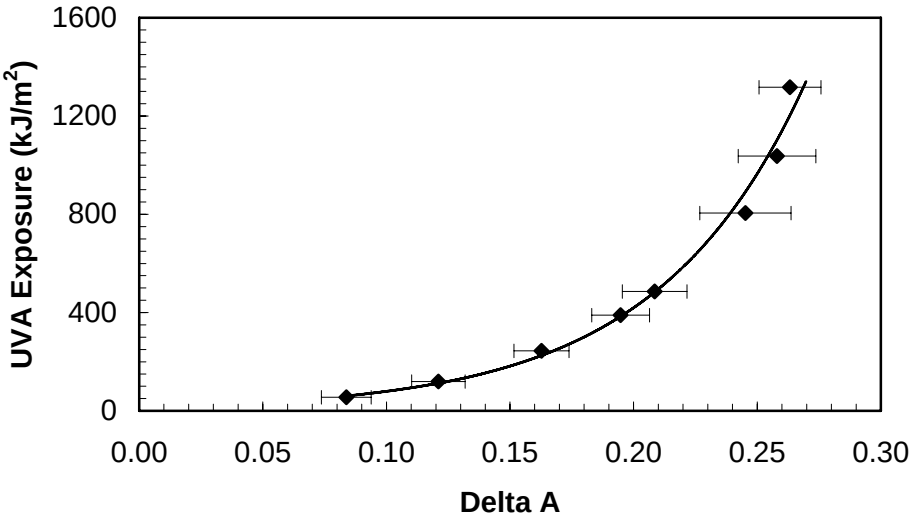


Figure 4 – Spectral absorbance of the UVA dosimeter measured pre-exposure and post-exposure to 20 min, 60 min and 90 min (from bottom to top curve) of solar UV on 17 January.

(a)



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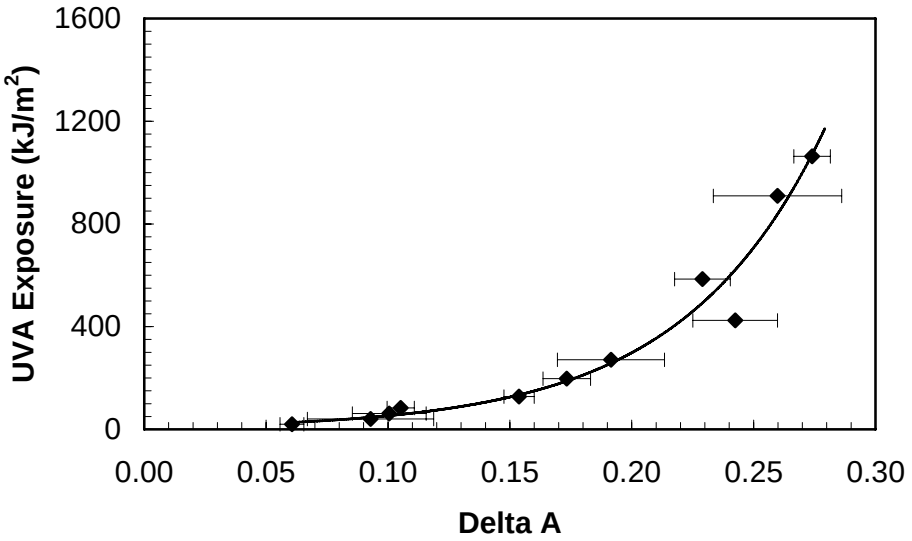

Figure 5 – (a) Low SZA calibration for the UVA dosimeter and (b) a high SZA calibration.